

# The Origins of Petroleum

by SIR ROBERT ROBINSON

Emeritus Professor of Chemistry,  
University of Oxford

Is the origin of petroleum organic or inorganic? In a discourse to the Royal Institution on November 11, Sir Robert Robinson argued that both theories are correct and that petroleum has a duplex origin. He went on to consider the carbonaceous constituents of certain meteorites and noted a possible implication relating to the origin of life on Earth.

THE genesis of petroleum presents problems primarily to chemists and geologists, but the subject has wider and fascinating implications. In fact it is to some extent dovetailed with the question of the origin of life on Earth. For this reason I would like to mention a rough scale of time.

The view at present held is that the planets were formed from the agglomeration of cold dust particles and larger masses in a rotating disk and that this occurred about 5,000 million years ago. There is no complete unanimity about the age of the Sun, but some authorities consider that it condensed about 6,000 million years ago. Rise in temperature occurred partly through compression due to gravitation, but much more by disintegration of radioactive elements.

Oil in commercially utilizable quantity is found in reservoirs in sedimentary rocks laid down at various times during the past 500 million years. The oldest correspond to the Cambrian Period. These reservoirs are formed by folds in the rock strata and the oil is confined by relatively impermeable rocks. Migration occurs from place to place.

## Chemicals of Oil

Petroleum is a complex mixture of hydrocarbons, largely of the general formula  $C_nH_{2n+2}$ , that is, they are members of the series of saturated alkanes. Hydrocarbons in petroleum frequently contain relatively less hydrogen, and are of the type  $C_nH_{2n}$ ,  $C_nH_{2n+2}$ , etc. These are ring compounds and not substances containing the double link. It is true that so-called aromatic hydrocarbons, such as benzene, are found in petroleum, but these are exceptionally stable and it is not easy to add hydrogen to their molecules.

Natural gas is of two kinds: (a) nearly pure  $CH_4$  (methane), which is almost certainly derived from decomposition of vegetation, as is the fire-damp of coal mines; (b) petroleum natural gas, also predominantly methane but containing significant amounts of  $C_2H_6$  (ethane),  $C_3H_8$  (propane) and  $C_4H_{10}$  (butane), decreasing in that order. This kind of gas is clearly the top end or lowest boiling part of the petroleum series. At the other end of the scale are petroleum wax and "earth wax", mixtures of solid hydrocarbons of higher molecular weight.

The earliest theory of the origin of petroleum was that of Mendeleev<sup>1</sup>, who postulated the formation of metallic carbides at high temperatures and their subsequent decomposition by water. These reactions afford methane, and the later processes, leading to higher hydrocarbons, were not considered in detail. Nevertheless, the idea held the field until strong evidence of biogenesis accumulated from about the early nineteen twenties. In 1946 Cox<sup>2</sup> summarized the evidence, which has since been much strengthened, as follows:

(i) Petroleum and bitumen are always associated with sedimentary rocks.

(ii) Practically all petroleum originated in brackish marine sediments.

(iii) High pressure is not necessary for the production of petroleum from the remains of organisms deposited with the sediments.

(iv) Higher temperatures than 200° C are not necessary and this is supported by chemical evidence.

(v) Petroleum was laid down in Cambrian and Ordovician strata and is found in all intermediate levels up to the Pleistocene. In support, Smith<sup>3</sup> found hydrocarbon oils in quite recent sediments. Later work, however, showed that these recent oils differed in important respects from typical "crude oil".

## Biogenic Hydrocarbons

The signature tunes of biologically produced hydrocarbons are based on four themes, each of which is loudly proclaimed in the recent sediments, but fades away and is only just audible in the most ancient "crude oils". First there is the optical activity of hydrocarbon oils<sup>4</sup>. This is found at peaks in the carbon number distribution; one of them is in the range of a possible sterol degradation product. It cannot be said that optical activity is absent in crude oil but it is at a very low level. It follows the rule and decreases with increasing age.

Second (noted, however, more recently than those that follow), there is a predominance of naphthenes with one and four rings in each molecule. The latter doubtless have a sterol or polyterpenoid origin.

Third, all mineral hydrocarbon oils contain porphyrins and these are both of plant and animal origin. The associated metal is commonly vanadium (as vanadyl), but nickel also occurs, especially in non-marine sediments<sup>5</sup>. Desoxophyllo-erythro-aetioporphyrin, related to chlorophyll, has been found in oils from Trinidad, Romania, the Caspian Sea and North and South America (locality not specified). Mesoporphyrin-IX, probably of animal origin, has also been found in some of these sources. The quantitative aspect has not been very carefully studied, but the crude oils contain less porphyrin than the more recent hydrocarbonaceous matter. The content of porphyrins in oils is very variable. Treibs heated the mesoporphyrin in a solvent for some weeks at 240° C and observed loss of carbon dioxide. He deduced that petroleum has never been heated much above 200° C. This conclusion has been frequently repeated as if it were gospel, but the experiment does not necessarily apply to conditions in which the carboxyl could be modified by salt or ester formation. The argument also, even if valid, cannot apply to the oil as a whole unless the porphyrin was present from the start.

The fourth and perhaps most convincing indication of biological origin is the odd-even distribution of *n*-alkanes as we ascend the C-number series<sup>6</sup>. The great odd predominance reflects the mechanism of formation from the fatty acid precursor:  $2R\cdot CO_2H \rightarrow R\cdot CO\cdot R \rightarrow R\cdot CH_2\cdot R$ ; or  $R\cdot CO_2H \rightarrow RH$ . The prominent peak which occurs at

$C_{29}$  cannot be derived from two molecules of a single even C-numbered fatty acid. The indication is that mixed ketonization of  $C_{17}H_{35}CO_2H$  and  $C_{11}H_{23}CO_2H$ , or of  $C_{15}H_{31}CO_2H$  and  $C_{13}H_{27}CO_2H$  occurred. The stearic-lauric combination is the more likely of the two.

A simpler hypothesis for the odd C-number hydrocarbons is decarboxylation of fatty acids of the  $C_{2n}$  series. Some of these have actually been isolated from Japanese and Polish petroleum<sup>7</sup>. Eisma and Jurg<sup>8</sup> have shown that when behenic acid ( $C_{22}$ ) is heated at 200° C for a long period in contact with clay, saturated hydrocarbons are produced. Rather surprisingly there was some synthesis of hydrocarbons containing more than twenty-one carbon atoms, though  $C_{21}H_{44}$  was a major product.

Although this odd C-number predominance is a clear sign of biological origin, it should be noted that it is not invariably observed in natural products. The waxes of certain Australian grasses studied recently in the C.S.I.R.O. Laboratories by means of mass spectrography seem to show a smooth odd-even distribution curve. Phytoplankton fatty acids have a much wider range than those of the higher plants, and Sir Ewart Jones and his colleagues have found even and odd numbered acetylenic acids as metabolic products of micro-organisms.

### Odd and Even Hydrocarbons

The hydrocarbons found in modern plants, as well as the straight chain *sec*-alcohols and ketones, conform to the odd C-number rule, for example, hentriacontane,  $C_{31}H_{64}$  (ref. 9). Chibnall *et al.*<sup>10</sup> found that the *n*-alcohols in plant waxes were of the even C-number series,  $C_{24}$ – $C_{36}$ ; the acids were also even C-numbered,  $C_{24}$ – $C_{34}$ , whereas the paraffins were odd C-numbered,  $C_{25}$ – $C_{37}$ . These authors concluded that the alcohols were the result of reduction of acids and the hydrocarbons were produced by decarboxylation of acids.

The odd predominance is all but absent in a crude oil. At intermediate ages it exists to a much less extent than in the recent sediments and in a well graded series from the youngest rock-source to the oldest. Fig. 1, due to Bray and Evans<sup>6</sup>, illustrates this situation. Martin, Winters and Williams<sup>11</sup> showed that a number of "crude oils" do in fact show odd predominance in the region  $C_{11}$  to  $C_{18}$ . But of forty "crudes" studied only fourteen showed odd predominance and this was marked in only seven of them. Despite this the majority was regarded as exceptional and in need of special explanation. Perhaps the contrary view is the more natural, but no consistent explanation of the exceptions springs to mind. The very inconsistency of them among themselves indicates intrusive elements which differ from case to case. Furthermore, in view of the evidence advanced by Calvin and others, of life in Pre-Cambrian times, it is not at all surprising that some of the most ancient "crudes" should show signs of biogenesis.

A further sign of biological origin is the proved occurrence of phytane and a lower homologue, pristane, in crude oil fractions<sup>12</sup>. These hydrocarbons contain the isopentane or isoprenoid unit skeleton, a characteristic feature of many natural products. Of course, these substances could also arise from polymerization of dienes. Optical activity, which I incline to believe will be found, would be decisive in favour of biogenesis.

A highly interesting observation has been recorded by Brunnock<sup>13</sup>. In certain African "crudes" there is a small but definite even C-number predominance in the  $C_{40}$ – $C_{46}$  range. Assuming a mixture of polycarbene generated hydrocarbons and biogenic hydrocarbons, the source of the small even predominance is probably the breaking of the chains of the bio-precursors and the recombination of the fragments so produced. This hypothesis fits in with the circumstance that fatty acids of the  $C_{40}$  and higher series have not been isolated from natural sources.

It is an interesting consequence of the simplest arithmetic that the random combination of two chains made by

scission of a longer one must lead to even C-number predominance.

During the past few years much attention has been devoted to the determination of the ratios of occurrence of the stable isotopes of carbon in mineral hydrocarbon, gas and oil, and in the presumed sources<sup>14</sup>. It is found that petroleum as a whole has a higher ratio of carbon-12 : carbon-13 than standard limestones and that the ratio decreases with rising molecular weight. It is significant that the lipids of an organism are richer in carbon-12 than the remainder of the carbon compounds. This is certainly consistent with the view that lipids represent a petroleum source. The fall in carbon-13 from lower to higher molecular weight may be a result of isotopic fractionation in the course of migration or to the established fact that a  $^{12}C$ – $^{13}C$  bond is easier to break than the  $^{12}C$ – $^{12}C$  bond.

While I admit the force of all these arguments and agree that the biogenetic theory is fully substantiated and is acceptable, I would point out that it may apply to only a part of the whole. No reliable standards are available which could be used to fix the expected magnitude of the various properties and effects already noted. Thus an undetermined proportion of the mineral hydrocarbon could be abiogenic despite the clear indications of biogenesis.

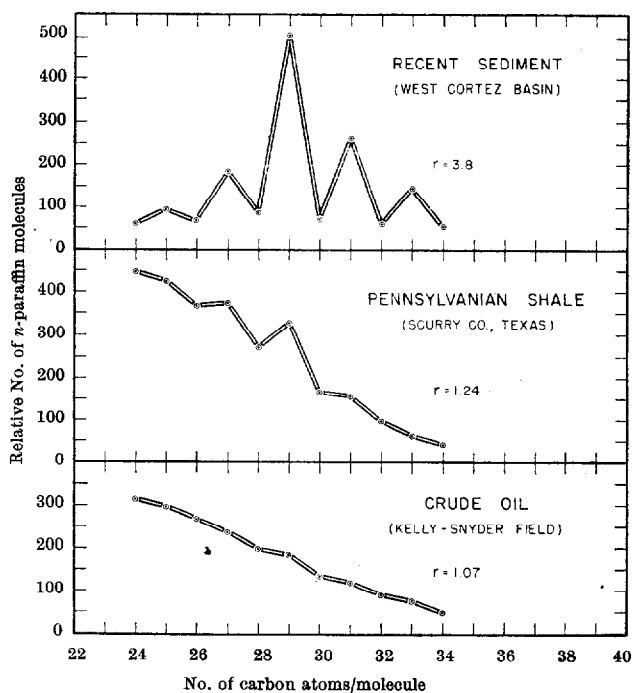


Fig. 1. Distribution of *n*-paraffins for a recent sediment, a marine shale and a crude oil.

It is thought that non-aqueous plants and animals did not exist in Ordovician times. The general view is that the source organisms were unicellular algae and foraminifera—usually phytoplankton. The awkward question is how can crude oil have arisen from such biological material? ZoBell<sup>15</sup> has advanced evidence which tends to show that bacteria can scarcely be responsible for changes effected at depth in the sedimentary rocks, though he has also demonstrated some remarkable reactions in this field. The reduction of carbon dioxide can, for example, be accomplished by lithotropic bacteria, provided a source of energy such as sulphur, ammonia or ferrous iron is present. It seems unlikely that bacteria are the main agents in the transformation of organic material into petroleum hydrocarbons. Their main chemical activity

will be evinced in the brackish waters before, or not long after, the formation of sediments. On a quantitative argument Whitehead has shown that radioactivity is unlikely to have produced much change in the organic constituents of the sediments (compare Brooks, E. T., in *The Chemistry of Petroleum Hydrocarbons*, 1, 91, 92; Reinhold, New York, 1954).

### Abiogenic Hydrocarbons

Some oil is found in fractures of igneous rocks in quite considerable amounts—about fifteen million barrels a year; however, it is probable that 99 per cent is found in the sediments<sup>16</sup>. The geological evidence has been discussed by Sylvester-Bradley<sup>17</sup>, who points out *inter alia* that in the case of sediments overlying igneous rocks the low specific gravity of oil favours its rise rather than its fall. In fact under marine conditions it would be hard to invent a plausible mechanism for the transfer downwards. From the point of view of the organic chemist, however, the most convincing argument for abiogenic oil is the composition of petroleum, especially the more ancient "crudes"<sup>18</sup>.

The progress of analytical techniques, particularly gas-liquid chromatography, has enormously facilitated the identification of individual hydrocarbons in petroleum fractions. As an example, a very complete analysis has been made of a Ponca City crude oil<sup>19</sup>. A valuable comparison of crude oils in respect of the composition of their lower fractions has recently been published by Martin and Winters<sup>20</sup>.

The outstanding results of analyses of crude oils are, first, that the main constituents in any carbon number are the normal paraffins gradually decreasing in concentration through all carbon numbers. This also applies to natural gas; the occurrence of substantial amounts of ethane and propane is noteworthy. Second, the branch-chain, cycloalkane, and aromatic constituents are just those which might arise from various known transformations of the *n*-alkanes<sup>21</sup>. Third, the absence of olefines and other easily reducible substances strongly suggests that the oils have been subjected to powerful hydrogenating conditions.

These points can be illustrated by reference to particular constituents, some of which are far removed from any known biochemical end-point. For example, *n*-hexane is always the major C<sub>6</sub> constituent. 2-Methylpentane and 3-methylpentane come much below it and in that order. This is the expected result of partial isomerization. Similar comparisons can be made in the C<sub>7</sub> series and the abundance of methylcyclopentane and methylcyclohexane relative to those of *n*-hexane and *n*-heptane, respectively, supply further examples. All the way through the picture of a hydroformed mixture of *n*-alkanes is maintained while many of the constituents have a very non-biological aspect—for example, neopentane, two of its homologues, and adamantane. The incorporation of nitrogen and sulphur is readily understood as the result of known catalytic processes. The products are pyridines, thiophenes, cyclic sulphides and other types which share the property of stability and relative non-reducibility. Crude oil has, indeed, all the appearance of a mixture of straight-chain alkanes modified under hydrogenating conditions.

Sir Ronald Holroyd has kindly furnished me (personal communication) with an account of the constituents of petrol made by hydrogenation of coal-creosote<sup>22</sup>. Many of the characteristic petroleum hydrocarbons (for example, methylcyclohexane) were identified, though there were also divergences. The comparison suggests similar effects of a process applied to different materials.

A noteworthy series of observations by Friedel and Sharkey<sup>23</sup> removes a difficulty, to which I had drawn attention in the past four years, concerning the methylpentanes and methylhexanes found in all petroleum. They were regarded as isomerization products from *n*-hexane and *n*-heptane, respectively. And in conformity

with anticipation, derived from laboratory experiment, more 2-methylpentane than 3-methylpentane was found on analysis. On the other hand, more 3-methylhexane occurs than 2-methylhexane and this was surprising (Figs. 2 and 3). This reversal has been found in many crudes and it always seemed difficult to explain. For the present purpose it is not necessary to understand the mechanism, because Friedel and Sharkey have found that the same reversal is characteristic of hydrogenated Fischer-Tropsch hydrocarbons. I regard this result as a most convincing argument favouring the part abiogenic theory.

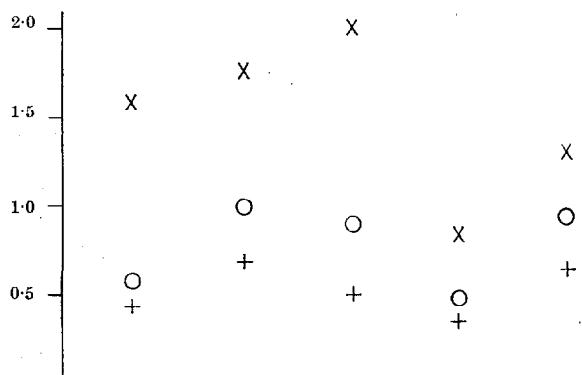


Fig. 2. Relative proportions of *n*-hexane (x), 2-methylpentane (O) and 3-methylpentane (+) in different specimens of petroleum. (After Bray and Evans, ref. 6.)

Adamantane, the molecules of which are cage-like, is found in small amount in petroleum. It can be synthesized by pyrolysis of hydrogenated *bis*-cyclopentadiene<sup>24</sup>. This is surely a typical abiological hydrocarbon.

One thing is certain, namely, that the biological constituents of petroleum, whether small or large in relative amount, have been submitted to strenuous conditions, for which long time at a lower level could be no substitute. For example, Mair and Martinez-Pico<sup>25</sup> isolated twenty-one compounds from the so-called trinuclear aromatic fractions of a heavy gas oil. Among these cyclopentenophenanthrene and a 1'- or 3'-methyl derivative were identified. It is true that these and others of the twenty-one compounds could be derived from sterols, but only at higher temperatures than those contemplated as possible in the sedimentary rocks.

### Biological Admixture

There is no reason to exclude biological additions to primordial oil long before the beginning of the deposition of the sedimentary rocks and possibly the time scale may be extended back into the thousands of million years. Crude oil has the make-up that would be expected of a Fischer-Tropsch mixture of normal hydrocarbons which has been mixed with material of biological origin and modified under hydrogenating conditions at an elevated temperature and in the presence of catalysts. Further biogenic material may well have been added later. Such a conception allows for various types of syntheses and degradations, the nature of which can be surmised from what we know of processes practised in oil refineries. The carbene hypothesis fits in most naturally with the formation of *n*-hydrocarbon chains and the Fischer-Tropsch process is a special case to which it is applicable.

Wilson and Johnson<sup>26</sup> have proved experimentally that methyl attacks molecules of fatty acids terminally when they are packed together in a monomolecular layer on water. This ingenious device discourages the formation

of branching chains. The process is envisaged as a possible extra-terrestrial synthesis of *n*-hydrocarbons and applied by Wilson<sup>27</sup> in a theory of the origin of petroleum and of the composition of the surface of maria on the Moon. For the former at least an atmosphere containing methane would be requisite as well as a source of energy, such as cosmic radiation, sufficient to produce the methyl radicals.

Another plausible theory has been advanced by Marx<sup>28</sup>. He suggests that hydrocarbons could be formed by hydrogenation of graphite, possibly by an electrolytic process. In addition to the usual straight-chains, Marx points out that branch-chains could be easily generated, and these could be sources of pristane and phytane.

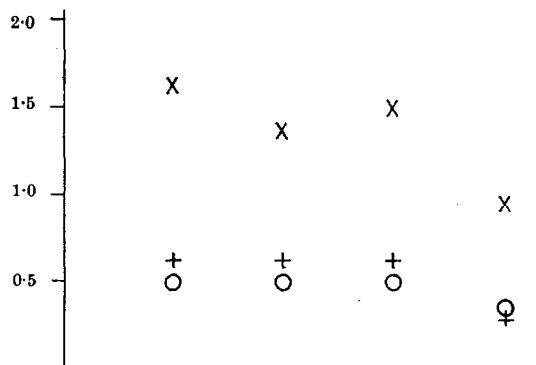


Fig. 3. Relative proportions of *n*-heptane (x), 2-methylhexane (O) and 3-methylhexane (+) in different specimens of petroleum.

As a comment I may add that the formation of certain metallic carbides from graphite could lead directly into the Fischer-Tropsch reaction sequence.

#### Origin of Life

The distribution of abiogenic oil and its association with living organisms present no difficulties. When oceans formed, a large amount of oil would probably have reached their surfaces and formed the carbonaceous substrate for plankton. The organisms and the oil would naturally have drifted to coastal regions and there become buried in sediments.

Even before the discovery of life-form residues in the carbonaceous chondrites the question of the origin of life on Earth seemed relevant to that of oil. Now, instead of thinking that oil, water and suitable minerals could form an environment in which an accident of synthesis could lead to life, we are more apt to contemplate those components as a substrate on which existing organisms could develop. Nevertheless, whether the origin of life was terrestrial or extra-terrestrial, the likely stages remain intriguing matter for speculation and the subject has been illuminated during the past decade by some striking experimental studies.

Miller<sup>29</sup> has shown that methane, water, ammonia, and oxides of carbon can be sources of protein-type amino-acids when suitably irradiated. Even more remarkable are the experiments of Harada and Fox<sup>30</sup>. Methane was passed through aqueous ammonia and then over catalysts such as silica gel at temperatures of 950° C or 1,050° C. Typical amino-acids were obtained in great variety. They included even aspartic and glutamic acids, proline, valine, leucine and isoleucine, phenylalanine and tyrosine. This extremely convincing discovery is of fundamental importance for the theory of the origin of life on this planet or even elsewhere.

It has been shown by Bahadur and Srivastava<sup>31</sup> that peptides can be formed by the irradiation of mixtures of amino-acids. Calvin<sup>32</sup> has been able to bring about many

syntheses of biological significance, using dicyandiamide as a dehydrating agent. The substances made include peptides, phosphates, pyrophosphates and other esters. It is of great interest that the coupling of dipeptide to tetrapeptide is faster than the formation of dipeptide from amino-acid. Thus the route to macropolypeptides is very open.

Cyanamide is a highly probable constituent of a primeval chemical complex, and therefore these results are most intriguing. As Calvin remarked in 1965, the field is extensive and is presently being further cultivated. He and his colleagues<sup>33</sup> have examined the constituents of some very old rocks, namely, the Nonesuch Shale about 1,000 million years old, and the Black Soudan Shale, which is about 2,700 million years old. Indubitable evidence of isoprenoid and sterane hydrocarbons was found in both these ancient rocks. It is scarcely possible to exaggerate the enormous significance of the discovery that such highly elaborated biochemical processes were in existence not so very long after the Earth had a relatively stable crust. It is hard to avoid the conclusion that the necessary evolution to that stage did not occur on Earth.

#### Meteorites

Meteorites can be classified into "irons" and "stones". The last include the carbonaceous chondrites, study of which has been pursued intensively during the past few years. The results are so dramatic that paradoxically they have not received the attention from the general body of scientists that they so richly deserve. The main reason for this can be expressed by one word—contamination. I intend to write at greater length on this subject in another place and will be content to state here that I am convinced that contamination cannot be the explanation of the whole of the results. The Orgueil meteorite fell in 1864 and the main mass and fragments were soon placed on various museum shelves. Its constituents have been studied by Nagy and by Claus and others<sup>34</sup> from almost every possible point of view. I am most impressed by the evidence of optical activity and the precautions taken by Nagy to eliminate sources of error.

I believe the inescapable conclusion is that life on Earth has evolved from organisms that were older than the Earth as we know it.

It has been suggested that the meteorites arose from the disintegration of a lost planet. But is it not more likely that they are unaccreted masses that might have formed such a planet? Furthermore, do they differ fundamentally from the masses that formed the Earth? It is recognized that the "stones" and "irons" correspond roughly to the outer and inner parts of the Earth.

The next step would be the assumption that evidence of chemical residues from organisms found in meteorites implies that such life was also present in the masses that formed the Earth. There is a way of escape here, because the organic residues found, say, in the Soudan Shales do not necessarily connote living organisms. The products could have been brought in without the life; however, this does not make a very consistent story. For one thing we are, in that event, still faced with the dilemma of accounting for full development of biochemistry in a relatively limited period of time.

The hypothesis that life came from outside has frequently been contemplated, for example, by Arrhenius, Oparin, Haldane, Bernal, Pirie and others<sup>35</sup>, but unless I am mistaken the idea has always been one of inoculation and it was usually mentioned for the sake of completeness and quickly rejected. What I now suggest is that a proto-planet, on which living forms existed, in the system of a proto-sun broke up and that life persisted in the fragments at a low temperature. When the solar system was formed, development occurred on Earth because the conditions, including the availability of oil, were favourable.

As Bernal<sup>26</sup> has already mentioned, the validity of such a theory would mean that our biochemistry extends beyond the Earth. In fact there may well be one biochemistry, just as we are already well assured there is one chemistry, throughout the universe.

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